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Rapid communication

Structural characterizations and magnetic properties of three new reduced molybdenum phosphates

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Abstract

Three new molybdophosphates, $[Co(dien)_2]\cdot(H_3dien)_6\cdot\{[CoMo_{12}O_{24}(OH)_6(HPO_4)_2(PO_4)_6][Co(Hdien)]_2[CoMo_{12}O_{24}(OH)_6(PO_4)_8]\}\cdot(dien)\cdot4H_3O\cdot5H_2O$ (**1**), $(H_3dien)_4[M Mo_{12}O_{24}(OH)_6(HPO_4)_4(PO_4)_4]\cdot10H_2O$ [M = Co for (**2**), Ni for (**3**); dien = diethylenetriamine], have been synthesized by employing hydrothermal method and characterized by single crystal X-ray diffraction. Compound **1** is built up of $Co[P_4Mo_6]_2$ units as the structural motif covalently linked by [Co(Hdien)] complex subunits to yield an unusual 1-D chain. Compounds **2** and **3** are isomorphic and both display covalent discrete $M[P_4Mo_6]_2$ cluster structures which are linked by the hydrogen bonds to form 3-D supramolecular networks. Both **1** and **2** display antiferromagnetic interaction and these three compounds all exhibit intensive photoluminescence.

Keywords: Hydrothermal synthesis; Polyoxometalate; Crystal structure; Organic–inorganic hybrid material

1. Introduction

The important developments of polyoxometalates (POMs) chemistry in recent years are exactly studies on syntheses, structures and functional properties for POMs with extended structures (1-D–3-D) based on discrete metal–oxygen cluster units covalently linked by transition metal complex fragments [1–3]. An important subclass of the POMs family is the reduced molybdenum phosphate based on the association of $\{Mo^V_2O_4\}$ fragments and PO_4 tetrahedra with structural range from zero to three dimensions, and in those intriguing structures $[P_4Mo_6]$ cluster units formed from $\{Mo^V_2O_4\}$ and PO_4 are firstly connected by metal–oxygen polyhedra producing $M[P_4Mo_6]_2$ building blocks which are further linked by transition metal complexes or metal–oxygen polyhedra to result in extended structures. To our knowledge, in reported to date 38 compounds containing $M[P_4Mo_6]_2$ building blocks there are 2 zero- [4,5], 15 one- [6–18], 8 two- [19–25] and 13 three-dimensional [9,10,14,26–34] structures. It can be seen that zero-dimensional compounds containing $M[P_4Mo_6]_2$ building unit are rare. In reported compounds involving the above-mentioned structure unit, there exist a variety of sandwich atoms M including Na^+ [6,16,24,27], Cr^{III} [23], Mn^{II} [7,14,15,22,25,28], Fe^{II} [4,11–13], Fe^{III} [20,26], Co^{II} [8,14,18,30,31], Ni^{II} [21,34], Zn^{II} [10,18,19,33] and Cd^{II} [5,9,10,29,32]. Here we report syntheses, structural characterizations, magnetic properties and photoluminescence of three new reduced molybdenum phosphates, $[Co(dien)_2]\cdot(H_3dien)_6\cdot\{[CoMo_{12}O_{24}(OH)_6(HPO_4)_2(PO_4)_6][Co(Hdien)]_2[CoMo_{12}O_{24}(OH)_6(PO_4)_8]\}\cdot(dien)\cdot4H_3O\cdot5H_2O$ (**1**) with covalent 1-D chain structure, $(H_3dien)_4[M Mo_{12}O_{24}(OH)_6(HPO_4)_4(PO_4)_4]\cdot10H_2O$ [M = Co for (**2**) and Ni for (**3**)] (dien = diethylenetriamine) possessing discrete $M[P_4Mo_6]_2$ cluster structures.

2. Experimental

2.1. Materials and instrumentations

All chemicals were purchased from commercial sources and used without further purification. Infrared spectrums

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of the title compounds were recorded with Perkin-Elmer SPECTRUM ONE FTIR spectrophotometer in the 400–4000 cm^{-1} regions using a powdered sample on the KBr plate. The elemental analyses were determined using a Perkin-Elmer 2400 series IICHNS/O elemental analyzer. Inductively coupled plasma (ICP) analysis was conducted on a Perkin-Elmer Optima 3300 DV spectrometer. XPS analyses were performed on a VG ESCALAB MK II spectrometer with a Mg-$K\alpha$ (1253.6 eV) achromatic X-ray source. Variable temperature magnetic susceptibility measurements were performed on a Quantum Design MPMS XL-5 SQUID magnetometer.

2.2. Synthesis of compound 1

A mixture of $CoCl_2 \cdot 6H_2O$ (0.1 g, 0.4 mmol), $Na_2MoO_4 \cdot 2H_2O$ (0.3 g, 1.2 mmol), dien (1.0 mL, 9 mmol), H_3PO_4 (1.0 mL, 12 mmol) and distilled water (12 mL) in a molar ratio of 2:6:45:60:3333 was neutralized to pH = 7.2 with ammonia water under stirring for 1 h and sealed in a 25 mL Teflon-lined stainless steel reactor, then heated at 170 °C for 3 days. After cooling to room temperature, the red-brown block crystals were isolated, washed with distilled water, and dried at ambient temperature. Yield: 0.18 g (55% based on Mo), IR (KBr pellets, ν/cm^{-1}): 943.74 for ν(Mo = O), 733.51 for ν(Mo–O–Mo), 1068.83 for ν(P–O), respectively. The features at 1518.86 and 1453.91 cm^{-1} are characteristic for the protonated dien. *Anal.* Calcd for $C_{22}H_{99.5}Co_{2.5}Mo_{12}N_{16.5}O_{66.5}P_8$: C, 8.23; H, 3.11; N, 7.21; Co, 4.60; Mo, 35.91; P, 7.73. Found: C, 8.01; H, 3.34; N, 6.71; Co, 4.47; Mo, 35.65; P, 7.58.

2.3. Synthesis of compound 2

Compound **2** was prepared under conditions similar to those of **1**; the only difference is the pH value of reaction system being 4.5. The red-brown block crystals were isolated. Yield: 0.22 g (70% base on Mo), IR (KBr pellets, ν/cm^{-1}): 947.29 for ν(Mo = O), 738.23 for ν(Mo–O–Mo), 1100.12 for ν(P–O), respectively. The features at 1508.22 and 1450.81 cm^{-1} are characteristic for the protonated dien. *Anal.* Calcd for $C_8H_{47}Co_{0.5}Mo_6N_6O_{36}P_4$: C, 6.27; H, 3.06; N, 5.48; Co, 1.92; Mo, 37.56; P, 8.08. Found: C, 6.45; H, 2.78; N, 5.57; Co, 1.87; Mo, 37.71; P, 8.13.

2.4. Synthesis of compound 3

Compound **3** was prepared under conditions similar to those of **1** with $NiCl_2 \cdot 6H_2O$ (0.1 g, 0.4 mmol) instead of $CoCl_2 \cdot 6H_2O$ in **1**. The reaction solution was neutralized to pH value being 5.0 with ammonia water. The red-brown block crystals were isolated. Yield: 0.15 g (47% based on Mo). IR (KBr pellets, ν/cm^{-1}): 948.76 for ν(Mo = O), 738.74 for ν(Mo–O–Mo), 1104.87 for ν(P–O), respectively. The features at 1510.84 and 1450.34 cm^{-1} are characteristic for the protonated dien. *Anal.* Calcd for $C_8H_{47}Mo_6N_6Ni_{0.5}O_{36}P_4$: C, 6.56; H, 2.90; N, 5.39; Mo, 37.57; Ni, 2.92; P, 8.09. Found: C, 6.27; H, 3.09; N, 5.48; Mo, 37.01; Ni, 2.87; P, 8.11.

2.5. Crystal structure determination

Single crystals of **1–3** were determined on a SIEMENS SMART CCD diffractometer by ω scan technique at room temperature using graphitemonochromated Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL 97 [35,36]. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms, except those of hydroxy groups and water molecules, were placed in calculated positions. The hydrogen atoms of hydroxy groups and water molecules were located from the difference Fourier maps and refined isotropically with the isotropic vibration parameters related to the non-hydrogen atoms to which they are bonded. For **1**, the C22 atom is disordered over two positions (C22 with SOF = 0.5 and C22′ with SOF = 0.5). In addition, the O1W was positional disorder with SOF = 0.5. Crystallographic and refinement details of compounds **1–3** are listed in Table 1, the selected bond lengths are listed in S-Tables 1 and 2.

3. Results and discussion

3.1. Synthesis

The principal difference of synthesis conditions for compounds **1–3** is pH value of reaction systems being different. Obtainments of **1–3** are under pH value of 7.2, 4.5 and 5.0 conditions, respectively. Appropriate high pH value of reaction system is beneficial to coordination for N atoms of dien to transition metals and results in formation of $[Co(Hdien)]^{3+}$, and thus leads to production of covalent 1-D chains of compound **1**. Acidic condition is favorable to protonation of dien while not favorable for coordination of N atoms of dien to transition metal atoms and hence leads to formation of covalent discrete cluster of compounds **2** and **3**. It can be seen from above-mentioned that pH value of reaction system is possibly one of important factors controlling structures of synthesized compounds.

3.2. Crystal structures of compounds 1–3

In compounds **1**–**3**, there are the common building unit $[P_4Mo_6O_{28}(OH)_3]^{9-}$ (denoted by P_4Mo_6). The structure of the P_4Mo_6 unit, which has no crystallographically imposed symmetry but has an approximate 3-fold axis, was first reported by Haushalter et al. in $[(H_2O)_3NaMo_6P_4O_{24}(OH)_7]^{2-}$ [6]. The structure of P_4Mo_6 in compound **1** is given in Fig. 1. As is usually observed, the Mo^V atoms are dimerized, forming $[Mo_2O_4]$ units. In the P_4Mo_6, three $[Mo_2O_4]$ units [Mo(1) Mo(2), Mo(3) Mo(4) and Mo(5) Mo(6)] are mutually connected by phosphate ligands and hydroxo groups. Such a linking mode results in P_4Mo_6 unit

Table 1
The crystallographic data for compounds **1–3**

Compound	**1**	**2**	**3**
Formula	$C_{22}H_{99.5}Co_{2.5}Mo_{12}N_{16.5}O_{66.5}\ P_8$	$C_8\ H_{47}Co_{0.5}Mo_6N_6O_{36}\ P_4$	$C_8H_{47}Mo_6N_6Ni_{0.5}O_{36}\ P_4$
Formula weight	3206.05	1532.50	1532.38
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	$P2_1/c$
a (Å)	15.5129(5)	13.2663(8)	13.2291(6)
b (Å)	15.5660(6)	21.9748(13)	21.7932(10)
c (Å)	20.5657(4)	15.6682(9)	15.5913(7)
α (deg)	77.182(2)		
β (deg)	71.296(2)	110.029(1)	110.058(1)
γ (deg)	60.797(2)		
V (Å^3)	4093.1(2)	4291.4(4)	4222.4(3)
Z	2	4	4
D_c(g cm^{-1})	2.601	2.370	2.411
F(000)	3141	2966	3003
GOF on F^2	0.946	1.038	1.060
Number of reflections collected	29741	23086	24424
Unique data ($I>2\sigma(I)$)	20041	8244	8473
R_1, wR_2 [$I>2\sigma(I)$]^a	0.0485, 0.1050	0.0296, 0.0826	0.0292, 0.0763
R_1, wR_2 (all data)	0.0860, 0.1193	0.0323, 0.0844	0.0312, 0.0776
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (Å^{-3})	1.586, −1.114	2.320, −0.925	1.906, −0.877

$^a R_1 = \sum||F_o|-|F_c||/||\sum F_o|$; $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum[w(F_o^2)^2]^{1/2}$.

being robust. The six molybdenum atoms are coplanar [mean deviations 0.0183 Å for from Mo(1) to Mo(6) and 0.0367 Å for from Mo(7) to Mo(12)], and display alternating short (approximately 2.597 Å) Mo–Mo bonds within the $\{Mo_2O_4\}$ units, and longer (approximately 3.489 Å) non-bonding contacts between the units, which is a common feature in cyclic arrangements based on dinuclear $\{Mo_2O_4\}$ units . The connections between the building units are edge sharing. The resulting hexanuclear ring encapsulates a central phosphate group [P(4)]. The central and the three peripheral phosphate groups lie on the same side of the plane defined by the six molybdenum atoms.

Compound **1** possesses novel 1-D chain structure. In compound **1**, the hexamer P_4Mo_6 units are bonded together with two types of cobalt atoms [Co(1) and Co(2)] which are crystallograhpically non-identical, forming two kinds of $Co[P_4Mo_6]_2$ clusters, standing form A and lying form B (Fig. 2 and S-Fig. 1). A form cluster and B form cluster are almost perpendicular to each other. Both cobalt atoms Co(1) and Co(2) lie in special positions [Co(1)$(0, \frac{1}{2}, \frac{1}{2})$ and Co(2)$(\frac{1}{2}, 0, 0)$] and their site occupancy factors are $\frac{1}{2}$. These both cobalt atoms are in octahedral coordination environment and each bridges two P_4Mo_6 units into a centrosymmetric dimer via six μ_3-O with average Co–O distance of 2.171 Å. As shown in Fig. 2 and S-Fig. 1, the clusters A and B are alternatively connected to each other through Co(3) complex cations $[Co(Hdien)]^{3+}$ by corner-sharing interactions of the P–O–Co(3) type to form an infinite castellated-like 1-D chain. To the best of our knowledge, in all reported to date compounds containing P_4Mo_6 units, 1-D chains [6–18] are all constructed from one kind of P_4Mo_6 clusters, while the 1-D chain consisting of two kinds of A and B P_4Mo_6 cluster in this paper are firstly found.

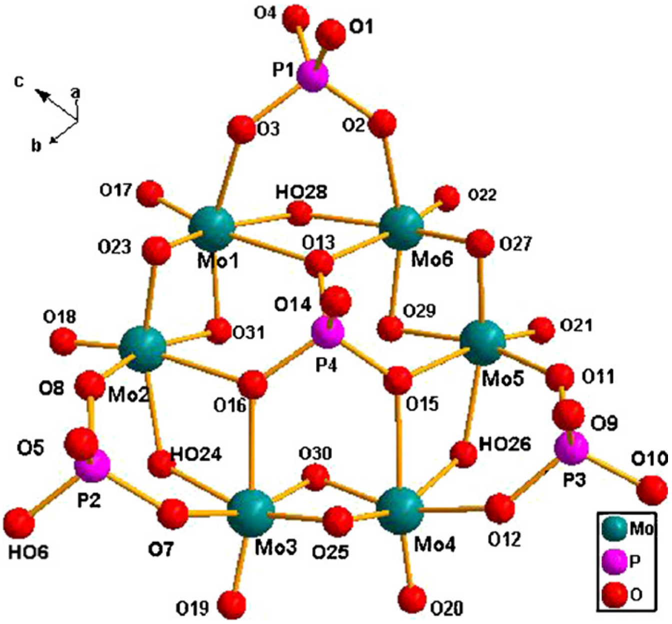

Fig. 1. Ball and stick representation of the anionic building unit P_4Mo_6 hexamer with atom labeling for compound **1**.

Co(3) atom in $[Co(Hdien)]^{3+}$ is bound to one dien and three PO_4 tetrahedra from two different P_4Mo_6 clusters (Fig. 2). Thus the Co(3) center is defined by two N donors from one dien ligands and three O atoms from two adjacent P_4Mo_6 clusters to form a distorted tetragonal pyramid [Co(3)-N, 2.095(7)–2.191(7) Å and Co(3)-O, 2.005(5)–2.103(5) Å] (Fig. 3a). In the square pyramid, the O(37), O(44), N(1), N(2) donors define a least-square plane with average deviation 0.046 Å, and the axial position is

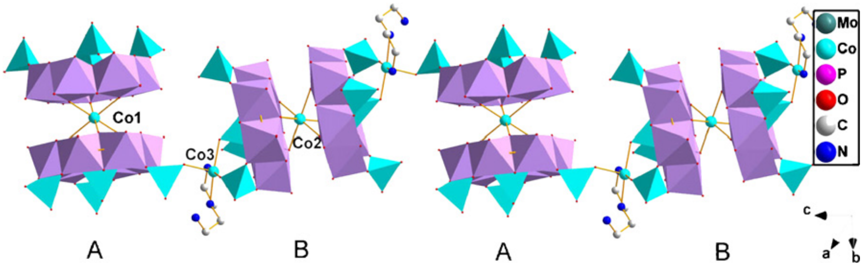

Fig. 2. Polyhedron representation of **1** showing a castellated-like chain in **1**.

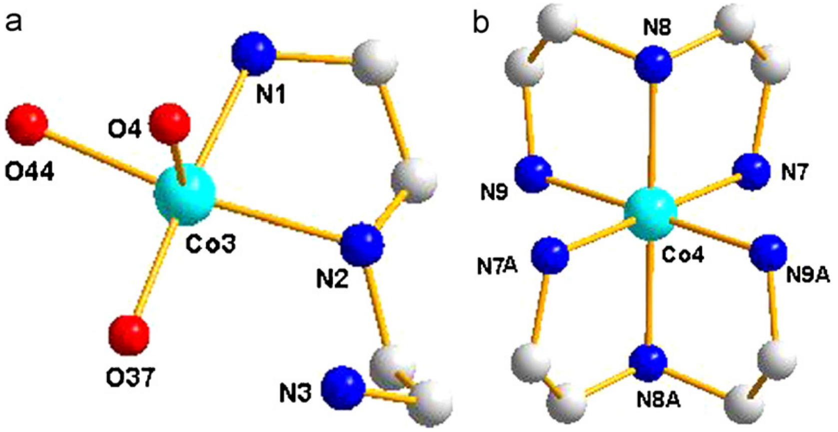

Fig. 3. Structures of $[Co(Hdien)]^{3+}$ (a) and $[Co(dien)_2]^{2+}$ (b) in **1** showing the unique coordination mode. All H atoms are omitted for clarity.

occupied by O(4) atom with distance 2.164 Å from the least-squares plane.

A second feature of compound **1** is that it contains isolated $[Co(4)(dien)_2]^{2+}$ cation (Fig. 3b). The Co(4) is the fourth kind of Co atom in **1** and crystallographically non-identical with Co(1), Co(2) and Co(3) atoms. Co(4) atom is at crystallographically symmetric center $(\frac{1}{2},\frac{1}{2},0)$ and its site occupancy factor is $\frac{1}{2}$. It is in a distorted octahedral coordination environment with six nitrogen donors from two tridentate dien ligands [Co(4)-N: 2.113(8)–2.161(10) Å]. There exist three kinds of dien molecules in compound **1**, coordinated dien with $\eta^{1,2}$ (Fig. 3a) and $\eta^{1,2,3}$ (Fig. 3b) mode and free dien. $\eta^{1,2,3}$ coordination mode [37–40] and free dien [5,41] have been reported, while $\eta^{1,2}$ coordination mode of dien in present paper is first reported.

Compounds $(H_3dien)_4[MMo_{12}O_{24}(OH)_6(HPO_4)_4(PO_4)_4]\cdot10H_2O$ [$M = $ Co for (**2**) and Ni for (**3**)] belong to isostructural ones and their structures consist of discrete cluster units $[M(P_4Mo_6)_2]^{6-}$, protonated diethylenetriamine H_3dien and lattice water molecules. The discrete $[M(P_4Mo_6)_2]^{6-}$ polyoxoanions form a 1-D supramolecular chain along a-axis in a head-to-tail way through hydrogen bonding between O(15) of $HP(3)O_4^{2-}$ and O(26) of $HP(2)O_4^{2-}$ groups for a $[M(P_4Mo_6)_2]^{6-}$ cluster unit as H-donors, respectively, with O(20A) of $P(1A)O_4^{3-}$ and O(22A) of $P(3A)O_4^{3-}$ group for a neighboring one as H-acceptors [for compound **2**: O(15)···O(20A), 2.630 Å; O(26)···O(22A), 2.635 Å; for compound **3**: O(15)···O(20A), 2.629 Å; O(26)···O(22A), 2.630 Å] (Fig. 4). Then each supramolecular chain is connected with four neighboring parallel ones to form a 3-D supramolecular network via hydrogen bondings between pentanuclear water clusters and O(8), O(22) and O(24) atoms of $[M(P_4Mo_6)_2]^{6-}$ cluster units [O(1W)···O(8), 2.986 Å; O(3W)···(22), 2.762 Å; O(1W)···O(4W), 2.727 Å; O(2W)···O(4W), 2.949 Å; O(3W)···O(4W), 2.687 Å and O(2W)···O(5W), 2.833 Å for **3**. Owing to disorder of a part of water in **2**, the related data of hydrogen bonds are not given] (Fig. 5a), or ones between the nitrogen atoms of H_3dien and related oxygen atoms of $[M(P_4Mo_6)_2]^{6-}$ cluster unit [N(1)···O(12), 2.775 and 2.782 Å; N(2)···O(24), 2.662 and 2.649 Å; N(3)···O(28), 2.799 and 2.808 Å; N(4)···O(28), 2.856 and 2.845 Å; N(5)···O(28), 2.705 and 2.688 Å and N(6)···O(27), 2.782 and 2.753 Å for **2** and **3**, respectively] (Fig. 5b). Existences of these two classes of hydrogen bonding interactions in **2** and **3** make their 3-D supramolecular network structures very stable.

3.3. Characterizations of compounds 1–3

3.3.1. Valence bond calculation

Valence bond calculations for compounds **1**–**3** (Table 2) confirm all Mo atoms being in reduced oxidation state (+5) [42]. Bond-valence sums of O(6), O(24), O(26), O(28), O(54), O(56) and O(58) for compound **1**, O(2), O(4), O(9), O(15) and O(26) for compounds **2** and **3** indicate them being hydroxyl O atoms.

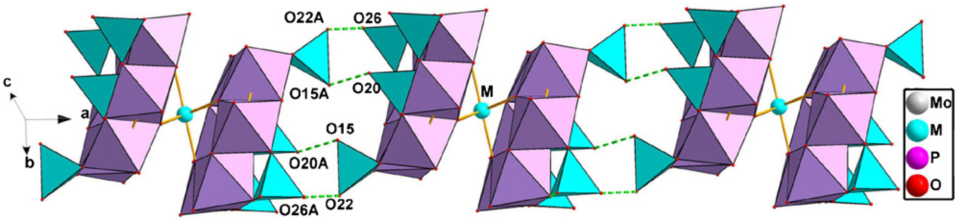

Fig. 4. 1-D supramolecular chain along *a*-axis, consisting of the discrete dimer $M[\mathrm{Mo_6(OH)_3(HPO_4)_2(PO_4)_2}]_2$ polyoxoanions in **2** ($M = \mathrm{Co}$) and **3** ($M = \mathrm{Ni}$).

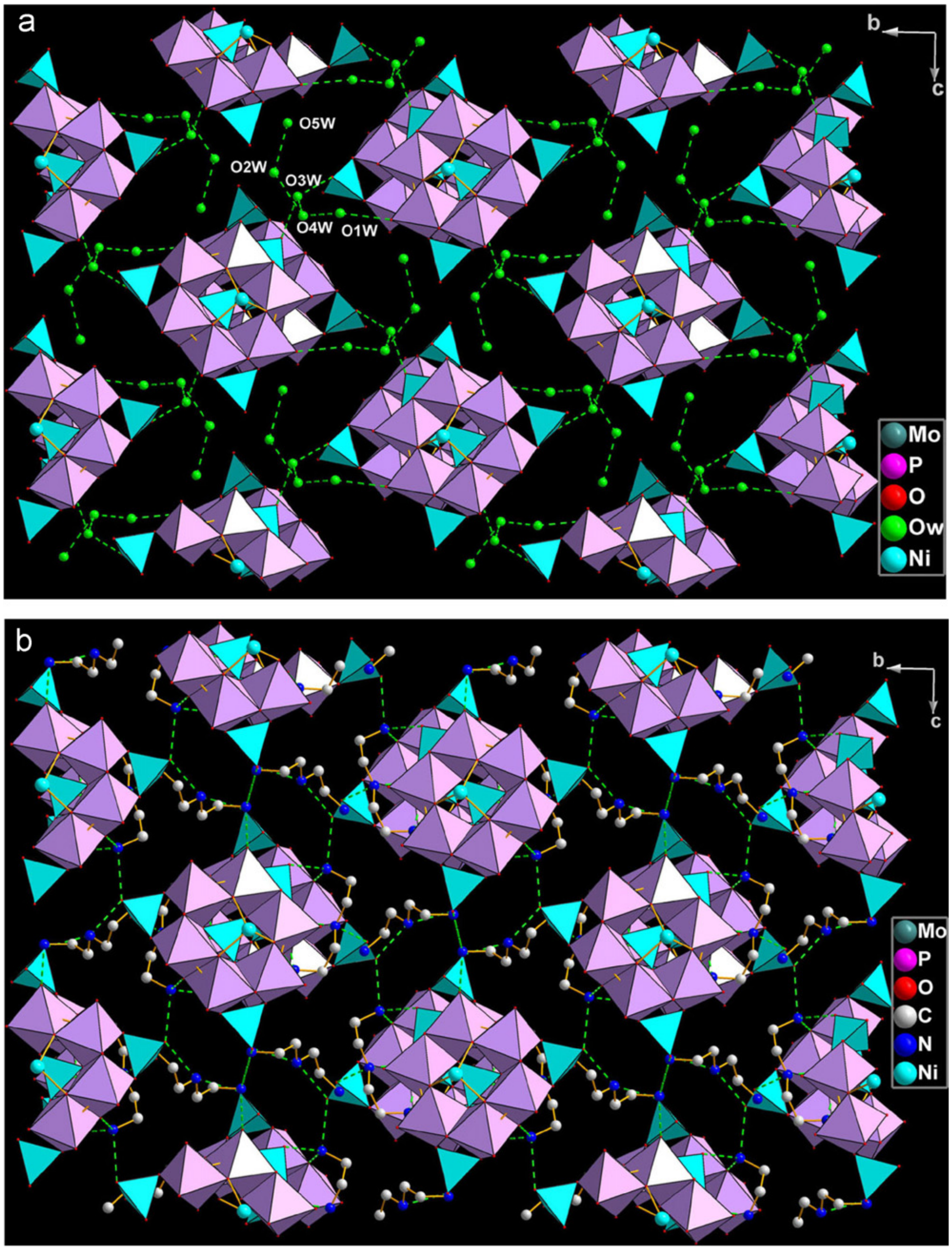

Fig. 5. 3-D supramolecular network along the *a*-axis direction via hydrogen bondings through (a) pentanuclear water clusters and (b) dien molecules for **2** and **3**, respectively.

3.3.2. XPS of compounds 1–3

XPS of compounds **1–3** (S-Fig. 2) give two peaks at 231.8 and 234.9 eV for compound **1**; 231.5 and 234.7 eV for compound **2** and 234.8 and 231.6 eV for compound **3** attributing to Mo^{5+} $3d_{5/2}$ and Mo^{5+} $3d_{3/2}$, respectively. The results further confirm the valence state of Mo atoms being +5.

*3.4. Magnetic properties of compounds **1** and **2***

The variable-temperature magnetic susceptibilities of **1** and **2** were measured between 4 and 300 K under 1000 G magnetic field. Fig. 6 shows the magnetic behaviors of **1** and **2** in the forms of the effective magnetic moments μ_{eff} vs. T. μ_{eff} of **1** and **2** continuously decrease as temperature is lowered from 7.77 μ_B at 300 K to 4.20 μ_B at 4 K for **1** and 3.65 μ_B at 300 K to 1.60 μ_B at 4 K for **2**, indicating the presence of the antiferromagnetic exchange interaction. The room temperature values of μ_{eff} being 7.77 μ_B for **1** and 3.65 μ_B for **2** are smaller, respectively, than only spin values being 8.21 μ_B of 2.5 Co^{2+} with $S = 3/2$ ($g = 2.68$) for **1** and only spin values being 3.67 μ_B of 0.5 Co^{2+} with $S = 3/2$ ($g = 2.68$) for **2**, indicative of antiferromagnetic coupling. Although valence states of Mo atoms are +5, owing to formation of Mo–Mo metal bonds, they have no contribution to magnetism of **1** and **2**. Unfortunately, it is too difficult to fit the experimental magnetic data of these two heterometallic high nuclearity spin systems using suitable theoretical models.

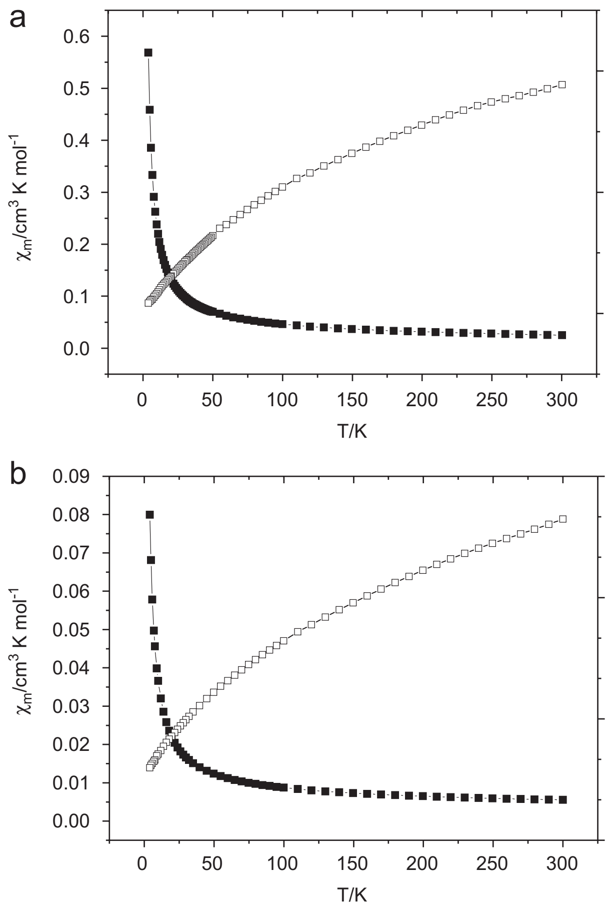

Fig. 6. The polt of χ_m(■) and μ_{eff} (□) vs. T for compound **1** (a) and **2** (b).

*3.5. Fluorescent properties of compounds **1–3***

Fluorescent spectra of compounds **1–3** in solid state were obtained on a LS 55 florescence/phosphorescence spectrophotometer at room temperature. The maximum emission band occurrs at 584 nm upon excitation at 407 nm for **1** (Fig. 7a). Similarly, compounds **2** and **3** exhibit intensive photoluminescence with an emission maximum at 537 nm upon excitation at 358 nm for **2** (Fig. 7b) and an emission maximum at 550 nm upon excitation at 373 nm for **3** (Fig. 7c). Based on emission spectrum of diethylenetriamine in room temperature exhibiting one emission maximum at 426 nm upon excitation at 353 nm (S-Fig. 3), the maximum emission bands of **1–3** do not belong to intraligands charge transfer while should be possibly assigned to ligand-to-metal charge transfer.

Table 2
Bond valence sums (Σs) for compounds **1**–**3**

1				2		3	
Atom	Σs	Atom	Σs	Atom	Σs	Atom	Σs
Mo1	5.02	Mo12	5.02	Mo1	4.92	Mo1	4.91
Mo2	5.02	O6	1.14	Mo2	4.98	Mo2	4.96
Mo3	4.91	O24	0.97	Mo3	5.00	Mo3	4.99
Mo4	4.93	O26	1.03	Mo4	4.94	Mo4	4.92
Mo5	5.02	O28	0.99	Mo5	4.90	Mo5	4.93
Mo6	4.90	O54	1.05	Mo6	4.91	Mo6	4.91
Mo7	4.89	O56	0.98	O2	1.01	O2	1.01
Mo8	5.09	O58	1.01	O4	1.09	O4	1.01
Mo9	4.96			O9	1.01	O9	1.03
Mo10	4.95			O15	1.16	O15	1.15
Mo11	4.87			O26	1.14	O26	1.16

4. Conclusion

Three new reduced heterometal molybdophosphates based on P_4Mo_6 building blocks, compounds **1–3**, have been hydrothermally synthesized. Compound **1** is the first covalent 1-D chain consisting of two kinds of forms of $M[P_4Mo_6]_2$ cluster units, standing forms and lying forms. Compounds **2** and **3** possess 3-D supramolecular network structures constructed from discrete cluster units $M[P_4Mo_6]_2$ (M = Co for **2** and M = Ni for **3**) via hydrogen bonding between pentanuclear water clusters and protonated diethylenetriamine with oxygen atoms of $M[P_4Mo_6]_2$ clusters. There exist antiferromagnetic interaction in **1** and **2**, and these three compounds all exhibit intensive photoluminescence. The fact that compound **1** was synthesized under weak basic condition while compounds **2** and **3** were synthesized under acidic condition shows that

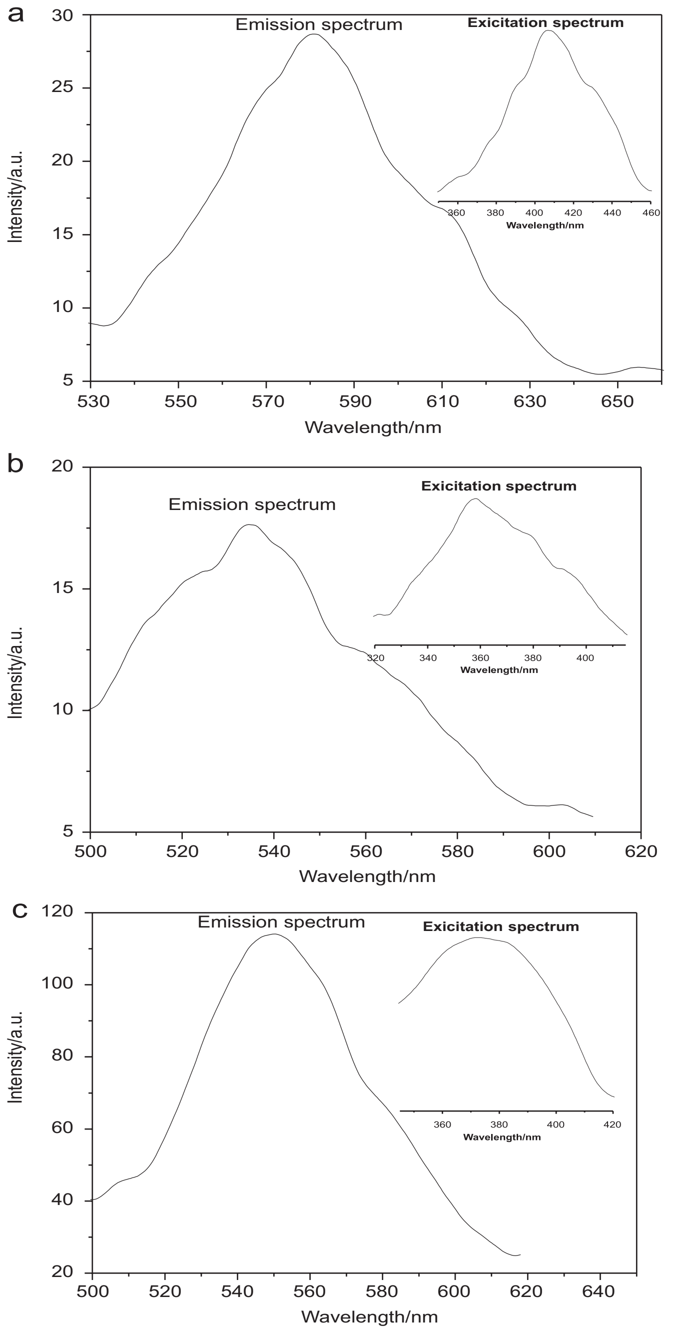

Fig. 7. Solid-state emission spectra of compounds **1–3** at room temperature.

pH value of reaction systems is possible one of important factors controlling structures of synthesized compounds.

Acknowledgments

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Appendix A. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 619862, 295070 and 627076, respectively. These data can be obtained free of charge at www.ccdec.cam.ac.uk/contas/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 IEZ, UK; fax: +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2007.02.015.

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